Argonne NATIONAL LABORATORY

Transformation of uranium under Fe(III)-reducing conditions: Reduction of U(VI) by biogenic green rust

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Environmental Remediation Sciences Program

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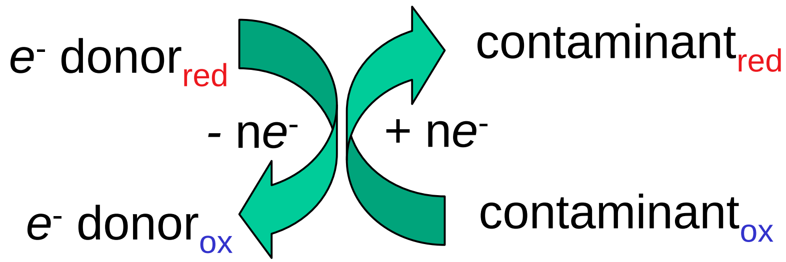
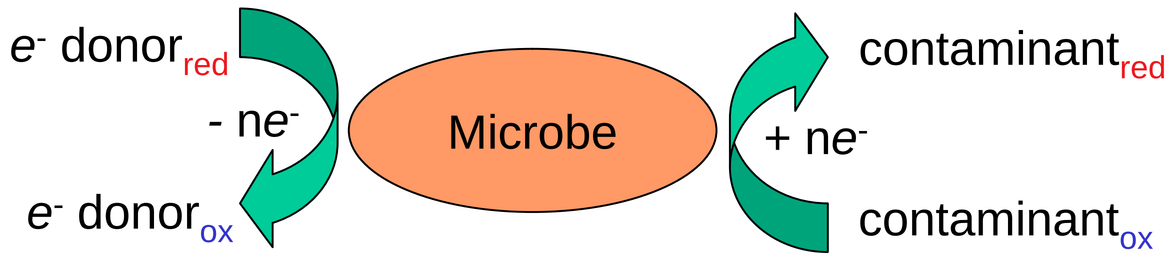
Abiotic, Microbial, and Microbially Mediated Reduction

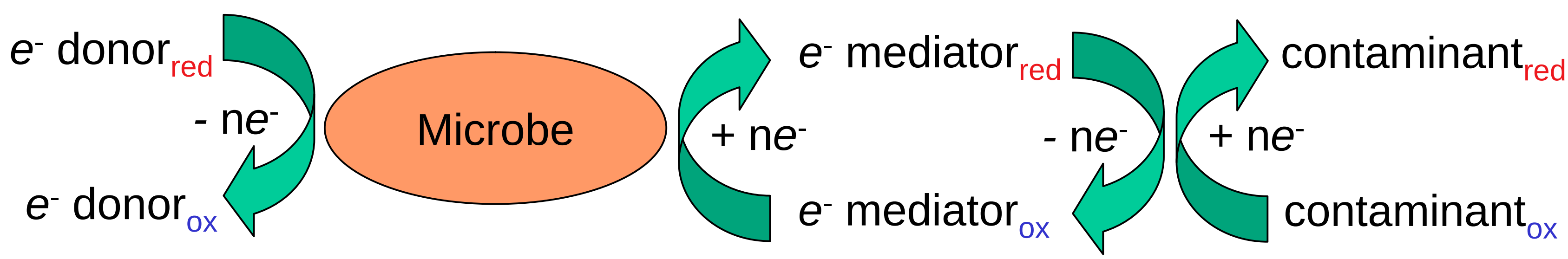
Abiotic



Microbial



Microbially Mediated



Dissimilatory Fe(III) Reduction

Organic C_{red}
H_2

- ne^-

Organic C_{ox}
H^+
CO_2

Soluble Fe^{III}

Ferrihydrite

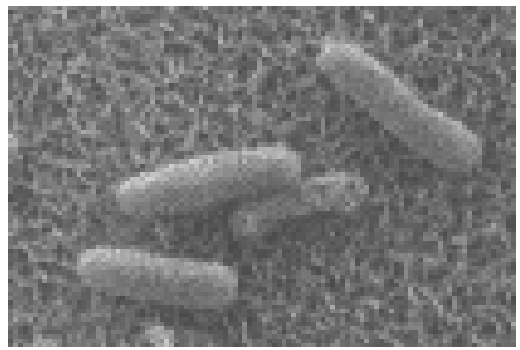
Hematite

Goethite

Lepidocrocite

Structural Fe^{III}
In Clays

Fe^{III}



Shewanella oneidensis MR-1

Fe^{II}

✓ Soluble Fe^{II}

✓ Sorbed Fe^{II}

✓ Magnetite

✓ Green Rust

Siderite

Vivianite

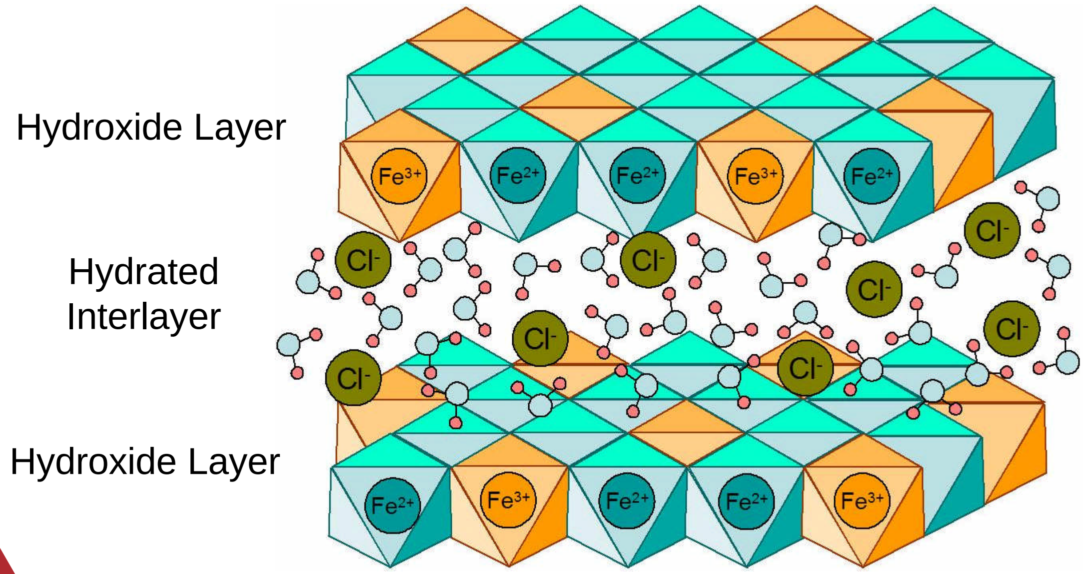
✓ Structural Fe^{II}
In Clays

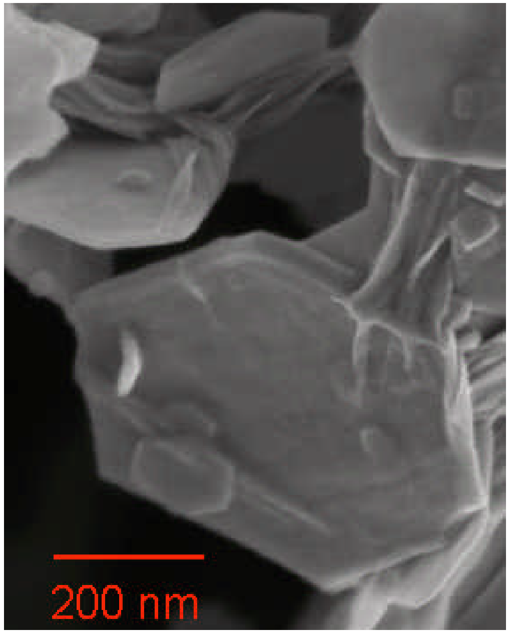
Energy

✓ Effective reductants for many organic and inorganic contaminants

Fe(II)-Fe(III) Hydroxide (Green Rust)

- Layered Structure
- General Composition: $[Fe^{II}_{(6-x)}Fe^{III}_{x}(OH)_{12}]^{x+}\ [(A)_{x/n}\bullet yH_2O]^{x-}$
- Formed via numerous biotic and abiotic processes
- Plays a central role in the redox cycling of Fe in many aquatic and terrestrial environments
- Capable of reducing many organic and inorganic contaminants (e.g., halogenated hydrocarbons, Se(VI), Cr(VII), Hg(II), Tc(VI), U(VI), etc.)





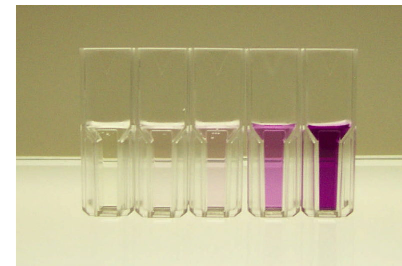
Dissimilatory Fe(III) Reduction

Experimental System

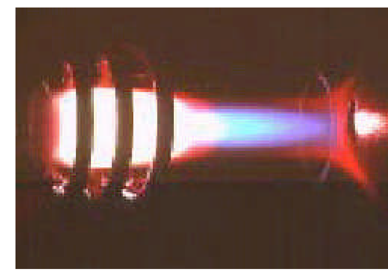
160-mL serum vial
100 mL Minimal Medium
75 mM e^- donor
80 mM Fe(III)
~5 $\times 10^9$ cells mL^{-1}

pH

Fe(II)



Total Fe/Fe(III)



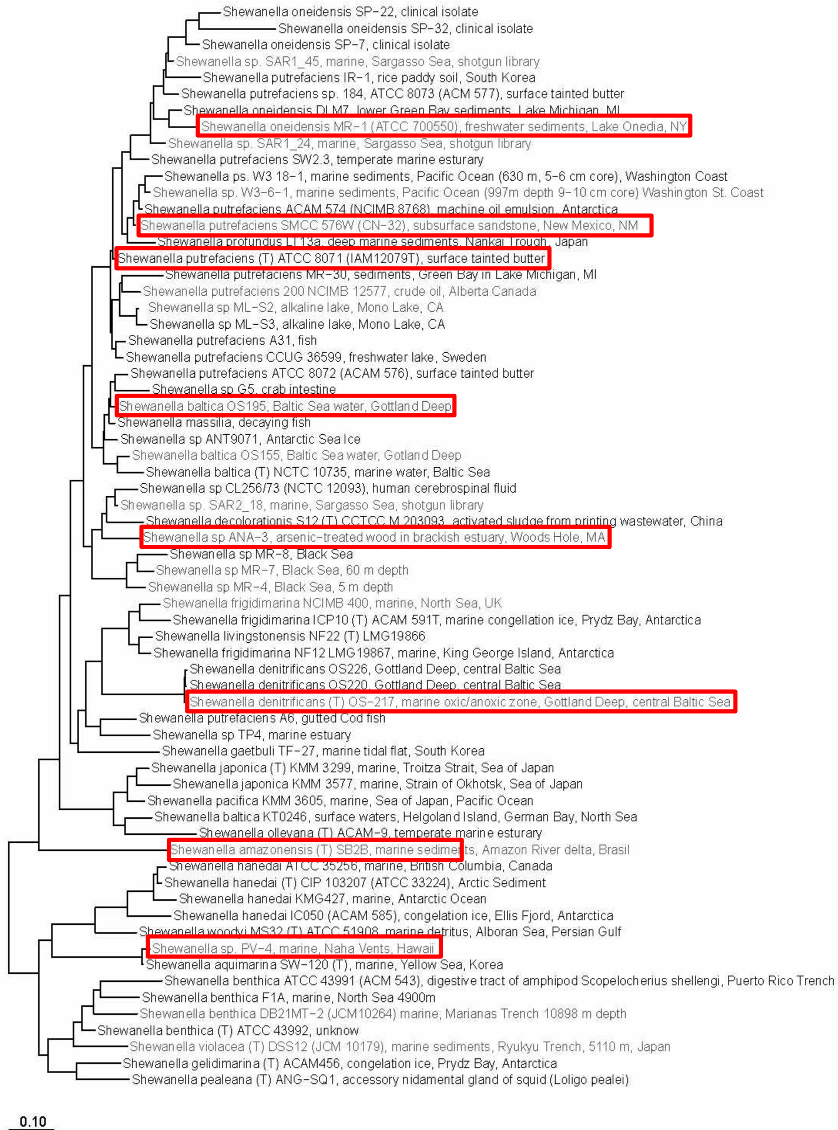
[e^- donor]

Solids

Shewanella *Surveyed for DIR of g-FeOOH*

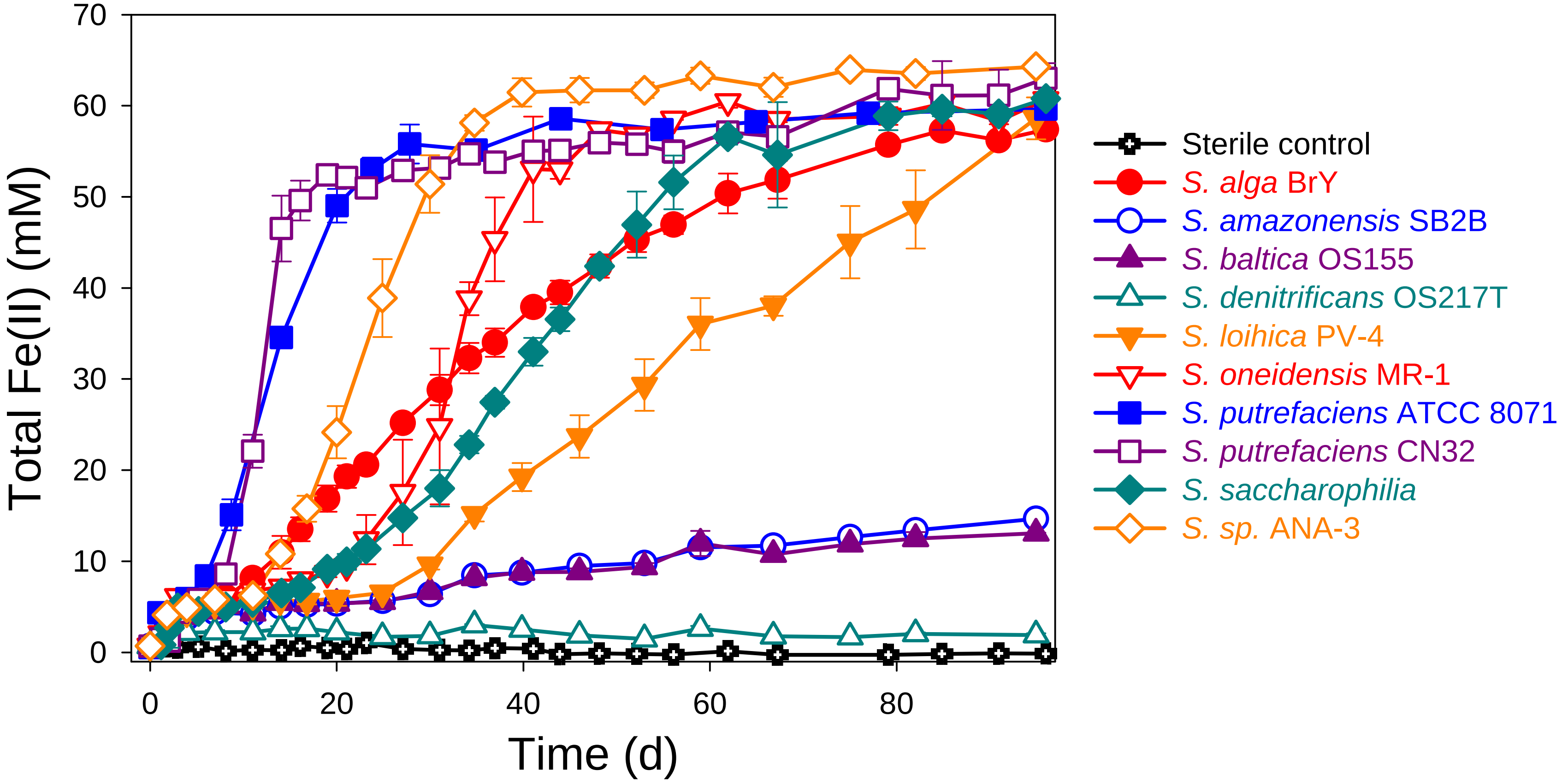
Shewanella

- g-Proteobacteria
- One of the most phylogenetically diverse genus of *Bacteria*
- Facultatively anaerobic
- Remarkable flexibility wrt range of e[-] acceptors for anaerobic respiration
- Physiological diversity reflected in range of habitats (mesophilic, psychrotolerant, psychrophilic, barophilic)
- Isolated from a broad range of environments (marine and freshwater, sediments, terrestrial subsurface)
- Commonly found at oxic/anoxic boundaries

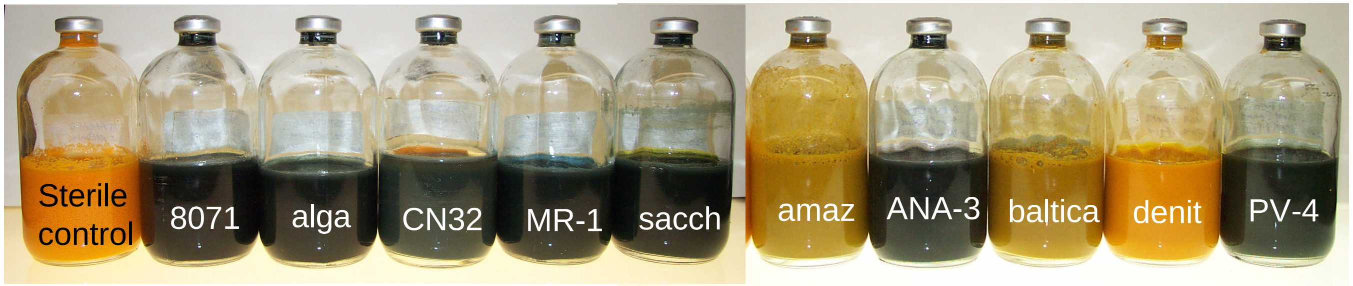


16S rRNA Tree courtesy of Jim Tiedje's group

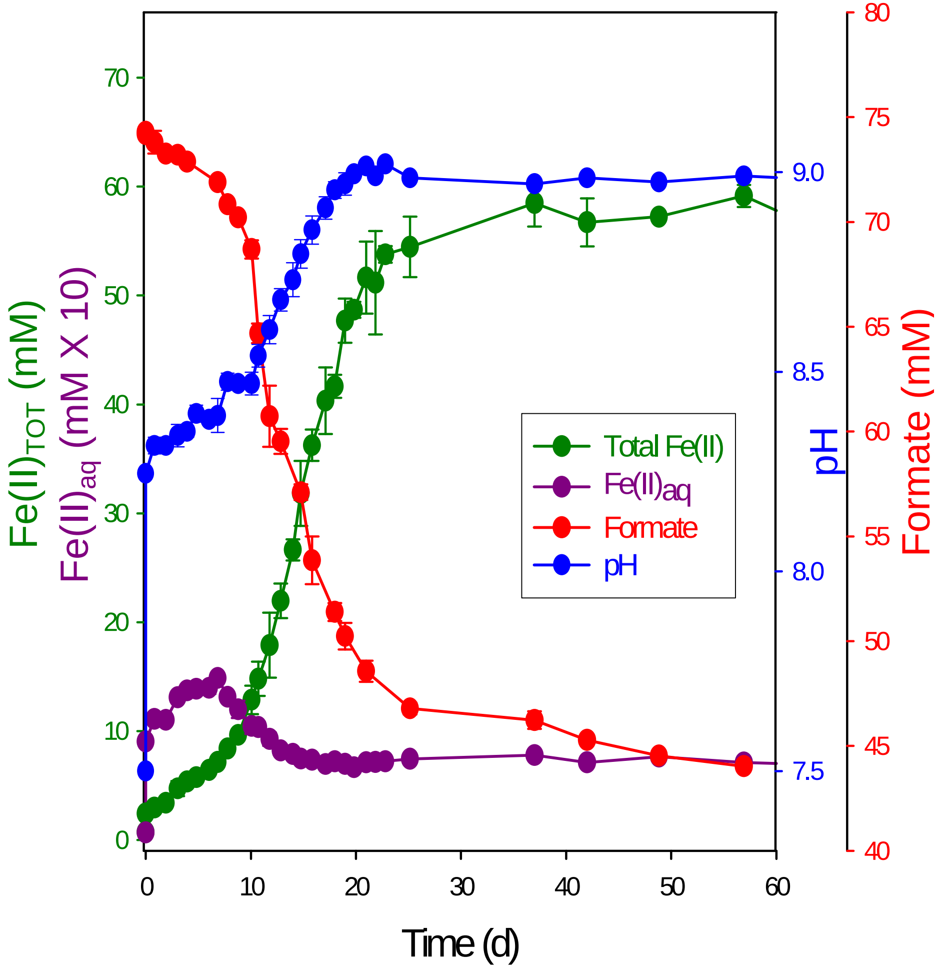
Reduction of Lepidocrocite by Shewanella *spp.*

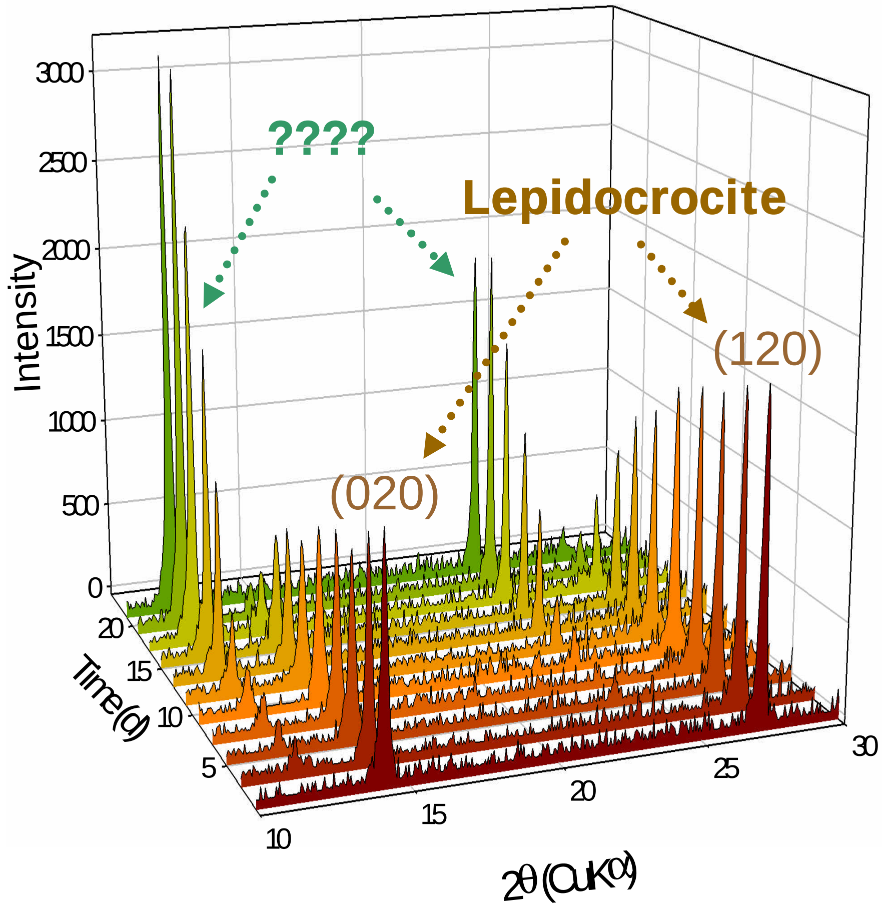


96 d



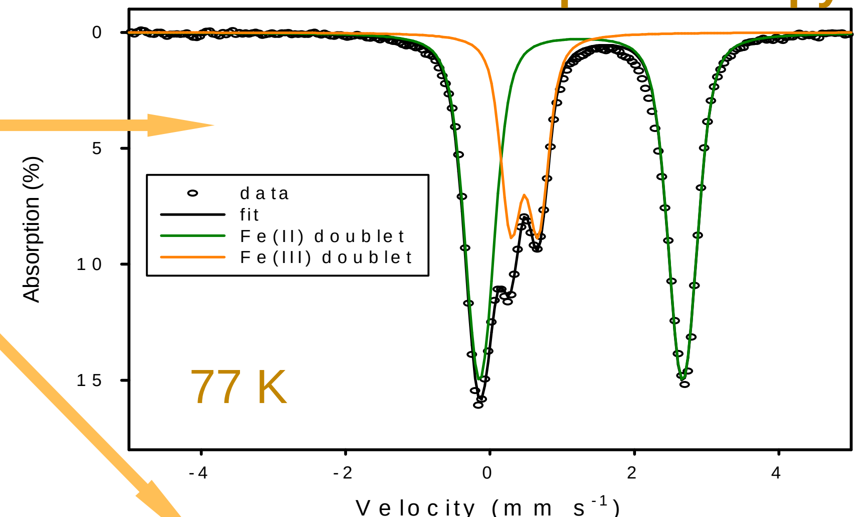
Lepidocrocite Reduction by CN32

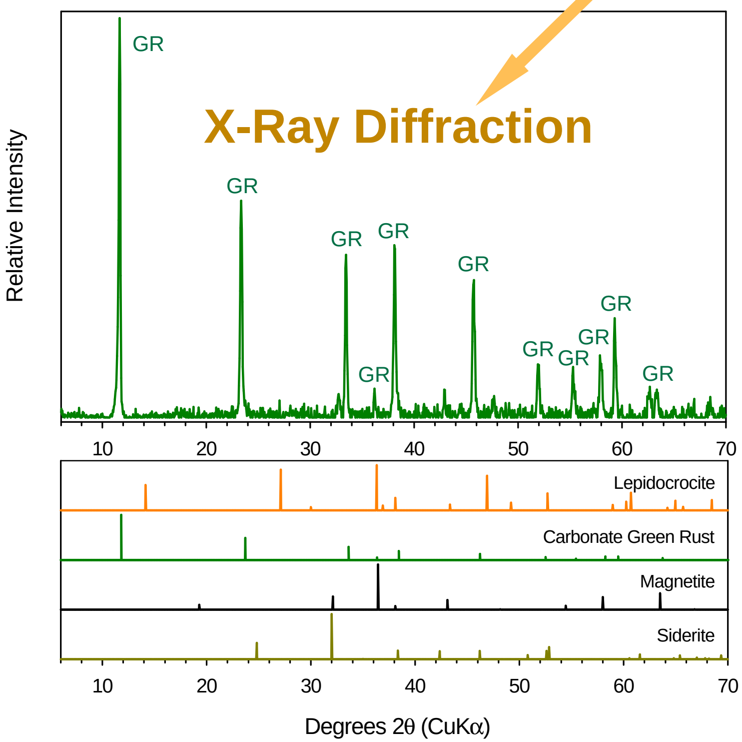


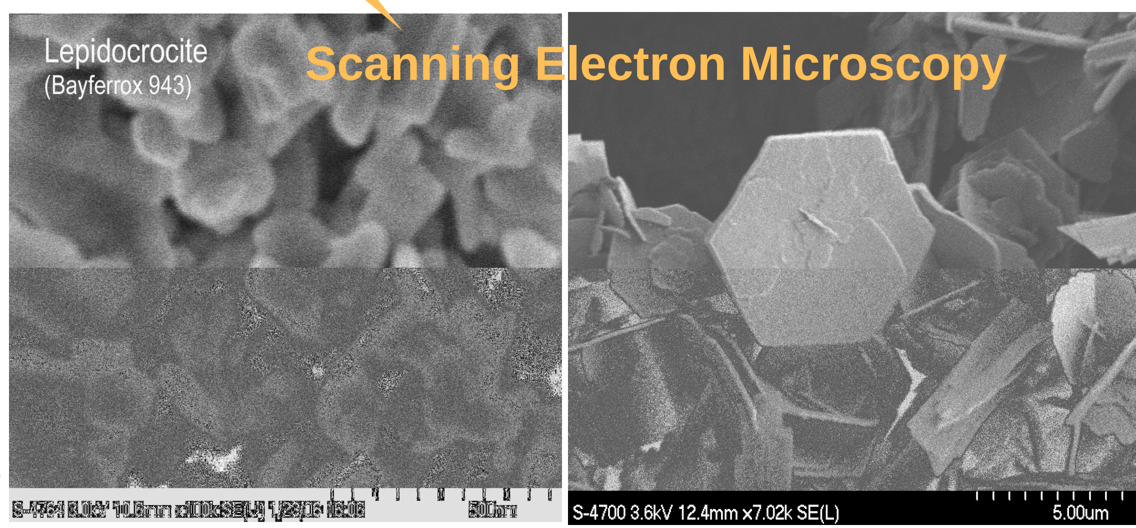


Characterization of Biogenic Solids

***S. putrefaciens* CN32**



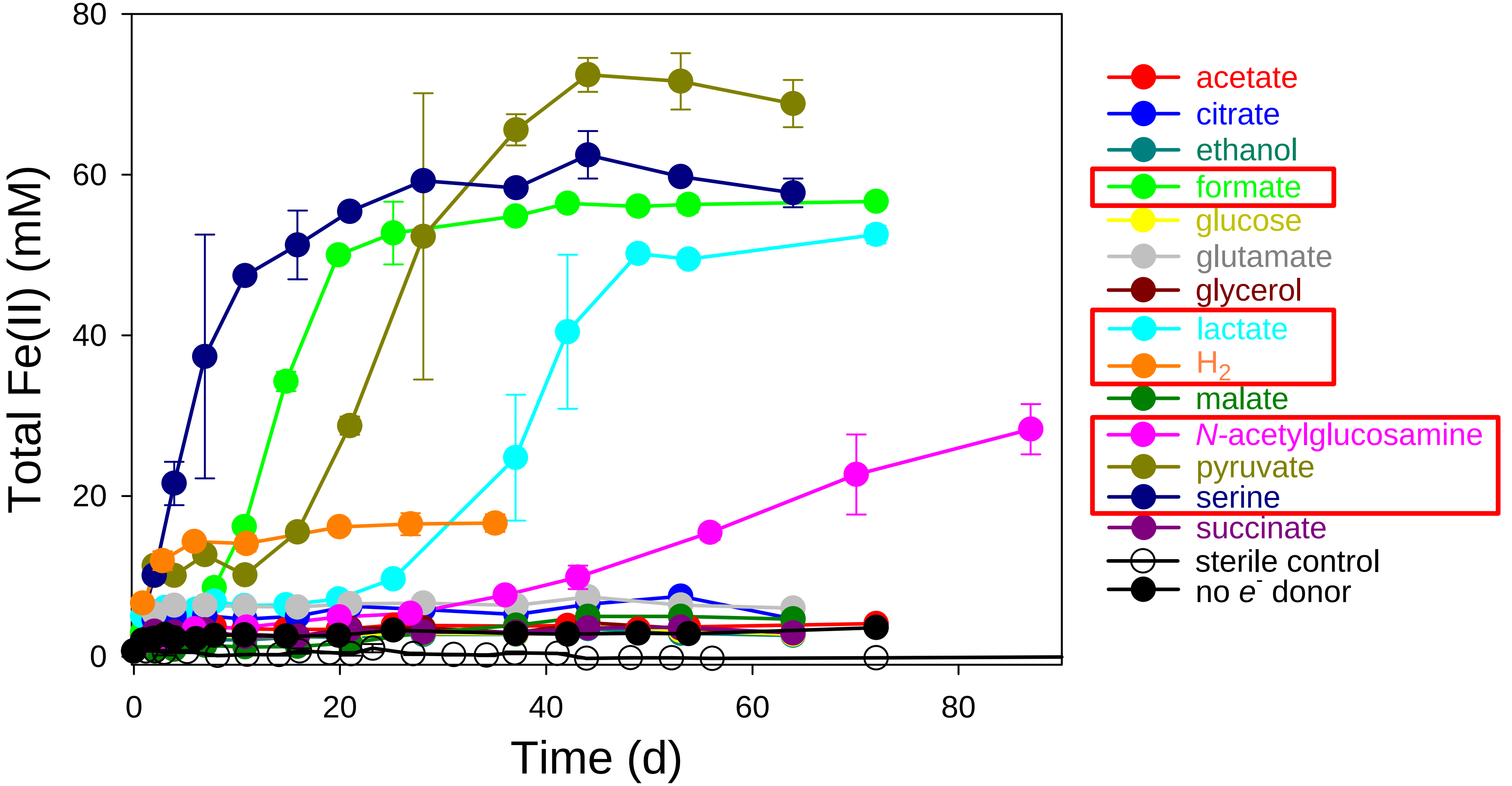




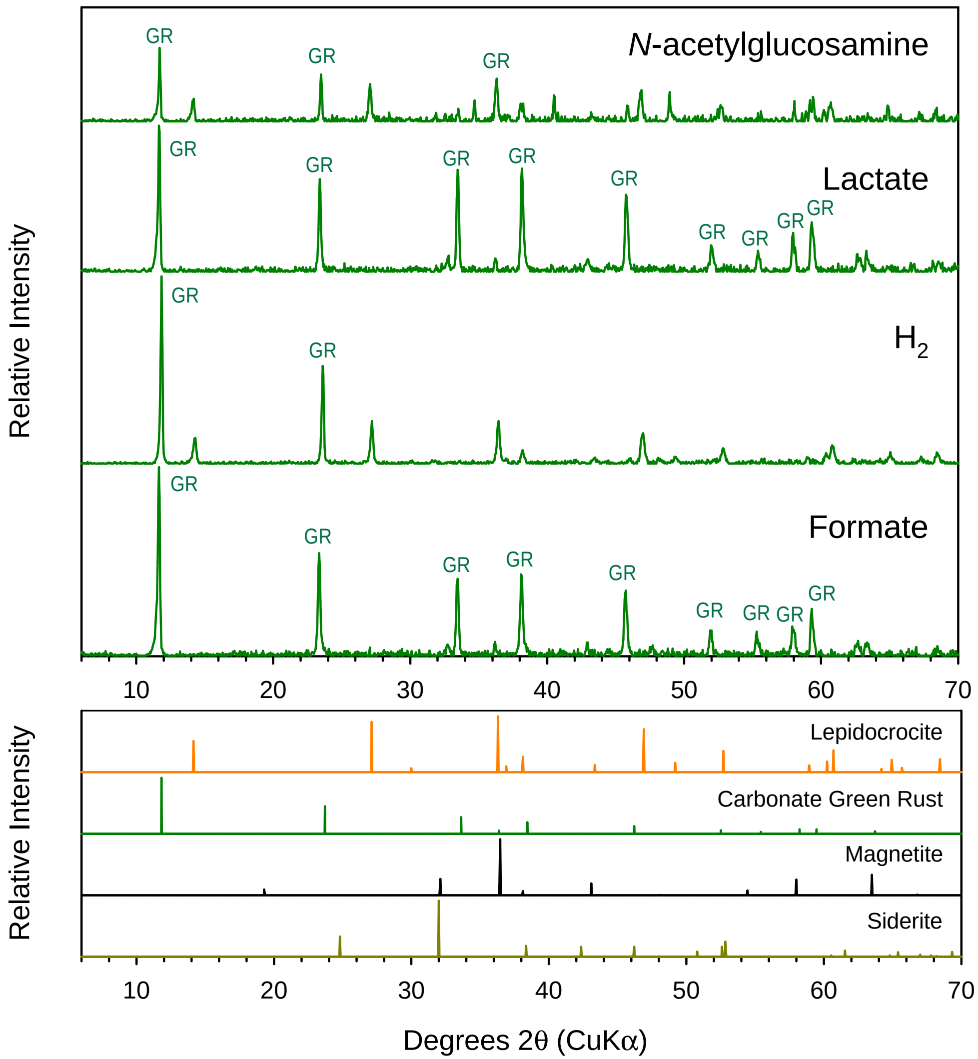
Green Rust produced by all but *S. denitrificans*

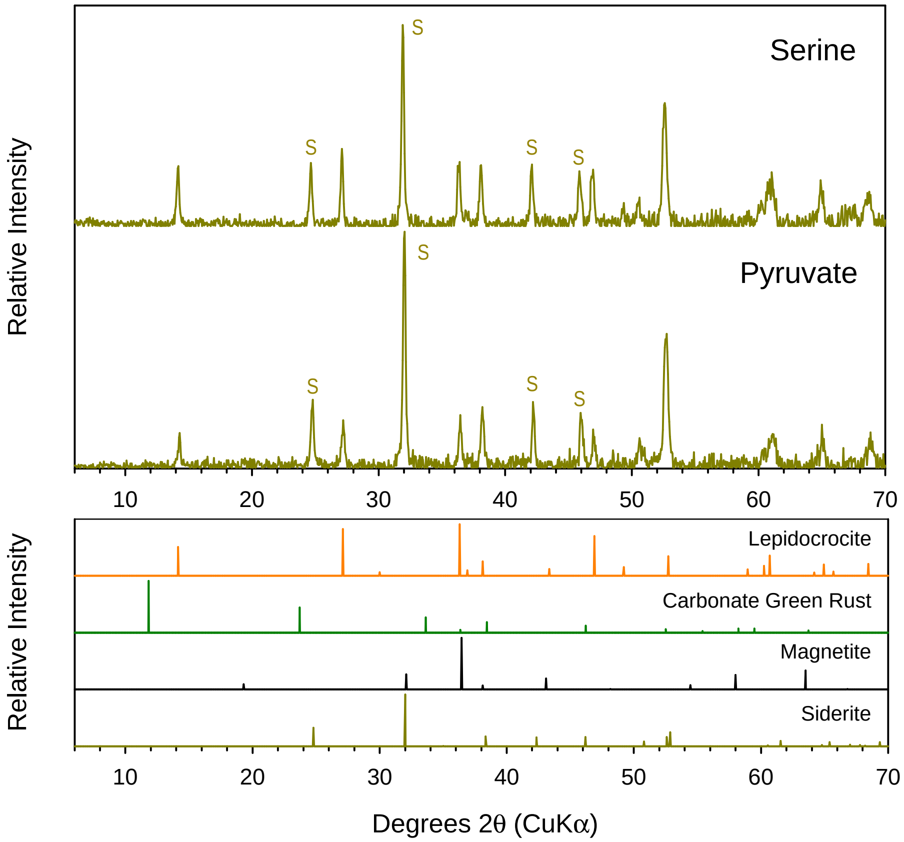
e⁻ Donor Effects on DIR of γ-FeOOH by CN32

Fe(II) production resulting from dissimilatory reduction of lepidocrocite by *S. putrefaciens* CN32



e- Donor Effect on Solid-Phase Fe(II) Products





U(VI) Interaction with Biogenic Green Rust

Experimental System

Biogenic GR
Pasteurized 70 °C
Washed/sonicated
58 mM Fe(II)

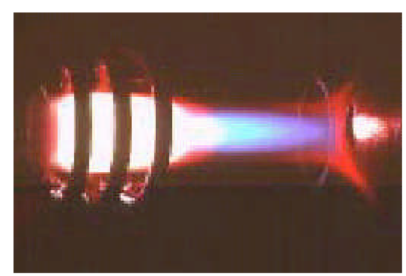
Add 500 µM U(VI)

pH

U speciation

U XAFS

Total U

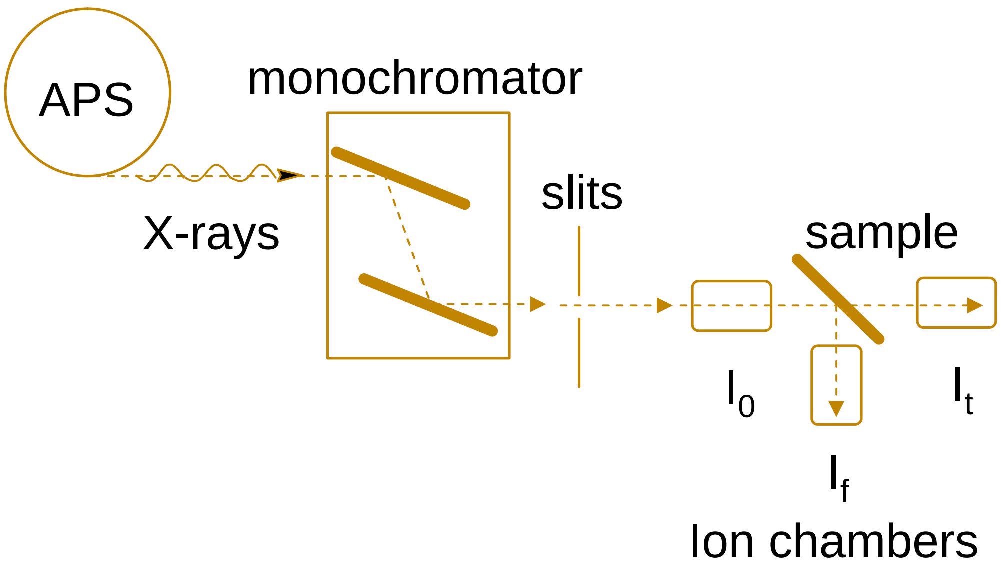


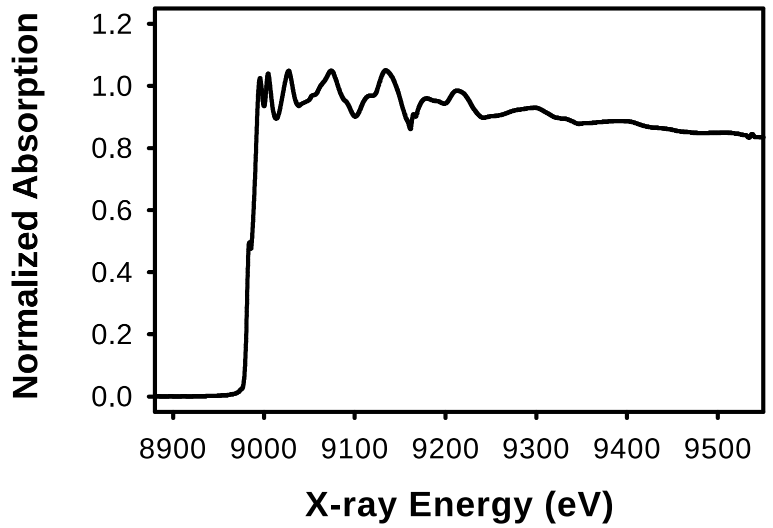
Within 48 h > 98% of added U associated with solids

Adsorption or Reduction??????

XAFS (X-ray Absorption Fine Structure)

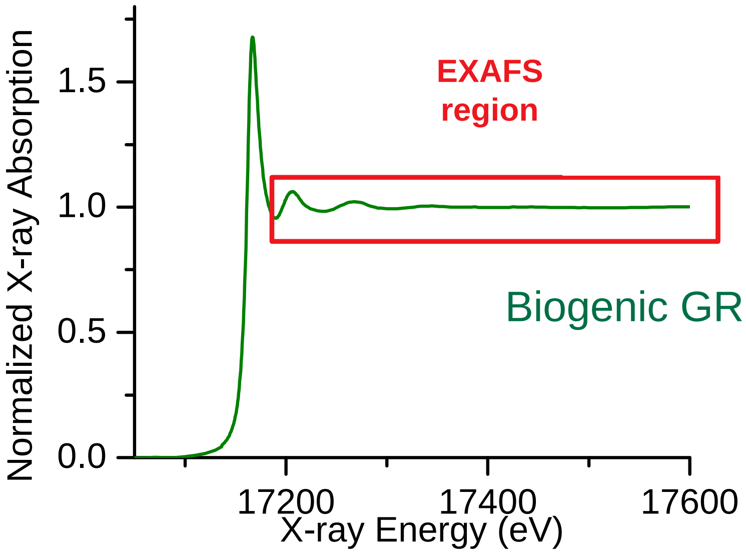
X-ray Absorption Fine Structure Spectroscopy

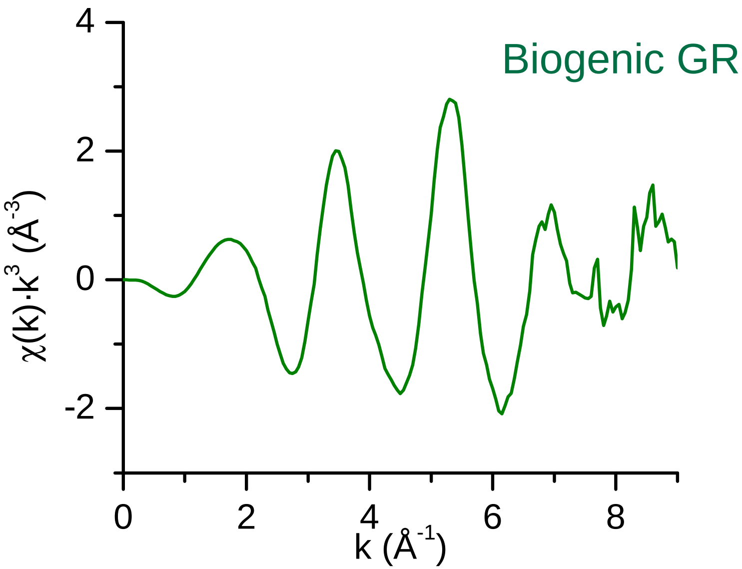


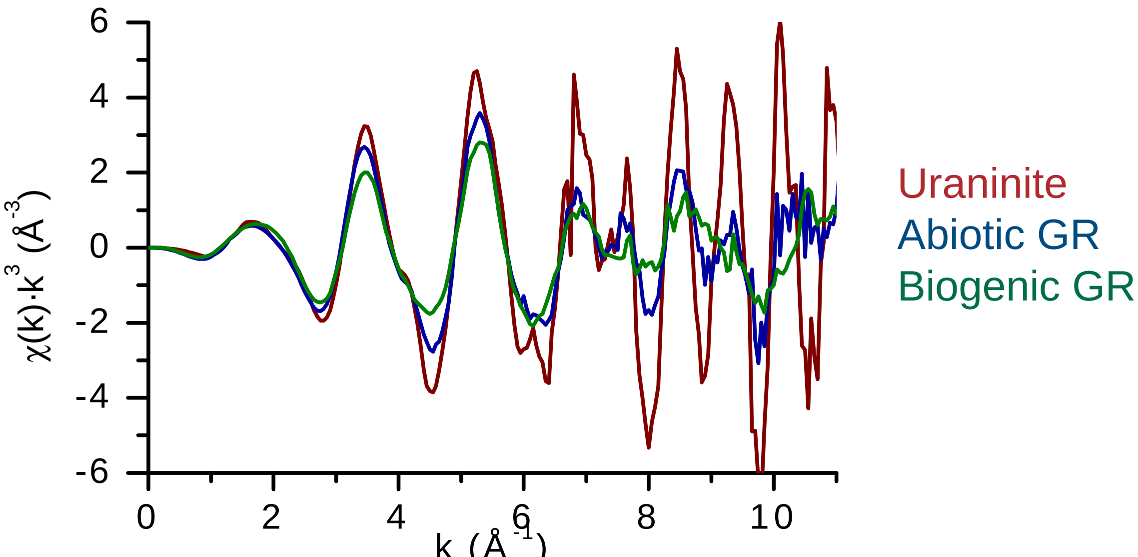


- **Short-range structural probe – provides information on oxidation state as well as the number, type(s), and distances of neighboring atoms (typically 1-2 "shells") along with an indication of structural disorder**

U(VI) Interaction with Biogenic Green Rusts



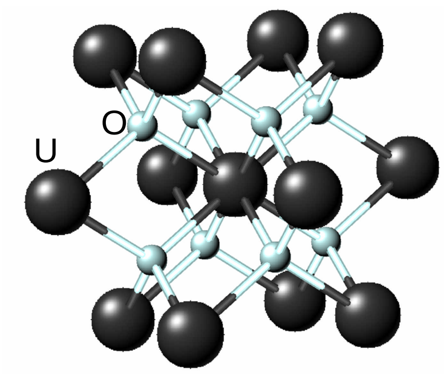




Modeling of EXAFS Data

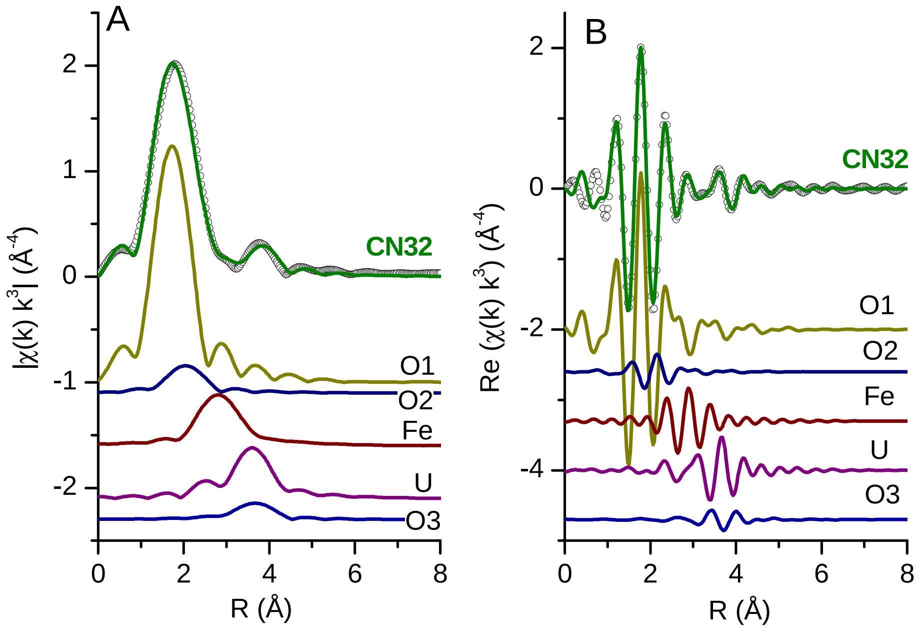
Model based on structure of uraninite (UO_2)

Neighboring atom	Microbe type	Number of neighbors	Distance to Neighbors (?)	Disorder in distance to neighbors (X10^{-3}?^{2})
U-O1	CN32	6.8 ± 0.4	2.31 ± 0.01	13.9 ± 1.7
	ANA3	7.2 ± 0.5		
	Alga	6.8 ± 0.4		
U-O2	CN32	1.2 ± 0.4	2.67 ± 0.05	13.9 ± 1.7
	ANA3	0.8 ± 0.5		
	Alga	1.2 ± 0.4		
U-Fe	CN32	1.9 ± 0.9	3.41 ± 0.02	10.4 ± 5.0
	ANA3	1.8 ± 0.7		
	Alga	2.0 ± 0.8		
U-U	CN32	3.3 ± 1.3	3.77 ± 0.03	10.4 ± 5.0
	ANA3	4.8 ± 1.4		
	Alga	3.8 ± 1.1		
U-O3	CN32	6.6 ± 2.5	4.43 ± 0.03	20.8 ± 10.0
	ANA3	9.6 ± 2.8		
	Alga	7.7 ± 2.2		



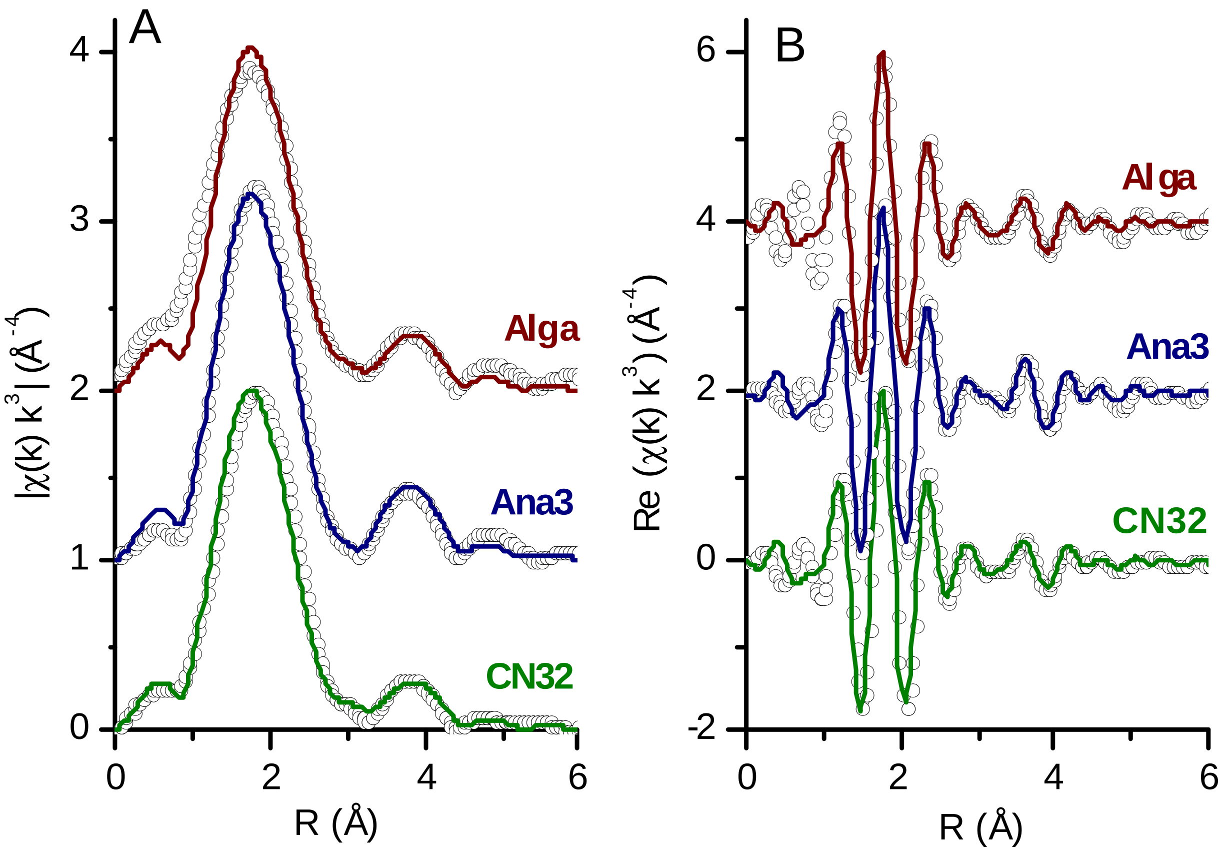
8 O at 2.35 Å

12 U at 3.87 Å



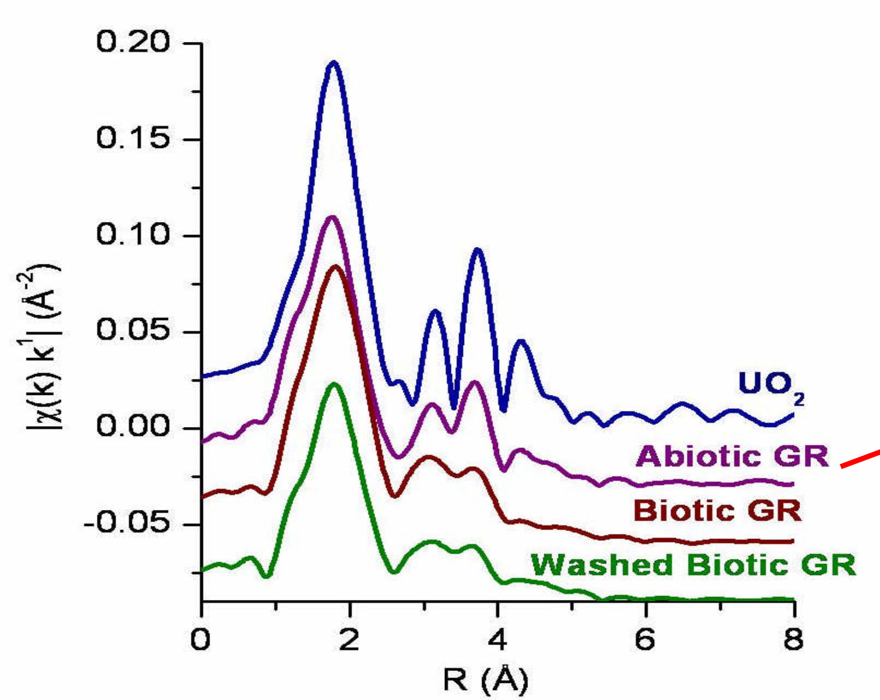
U(IV) structure in U-BioGR is <u>similar</u> to nanoparticulate uraninite (UO_2)

Comparison of Shewanella *species*

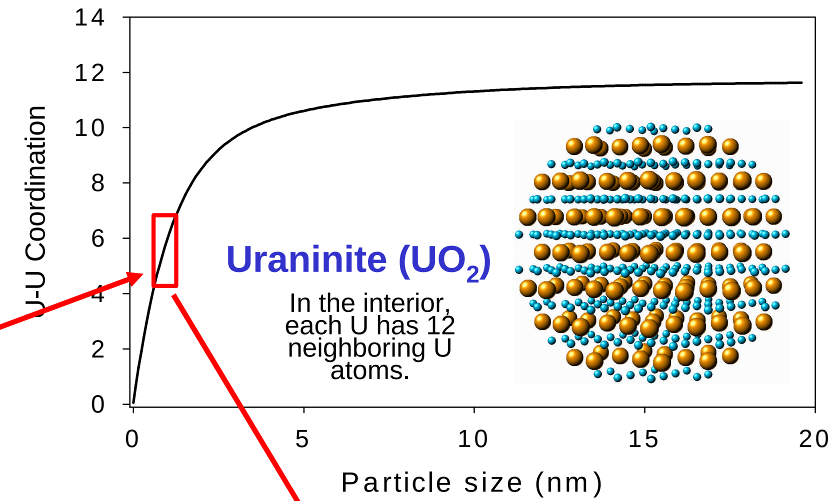


Results similar with green rusts formed by different species

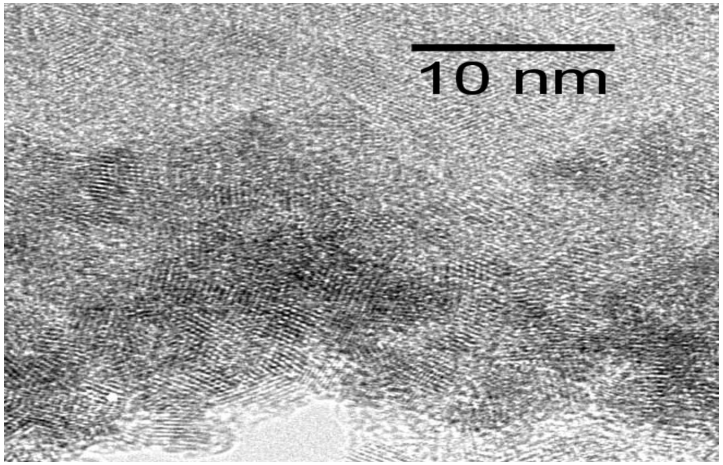
U(VI) Reduction by Green Rust

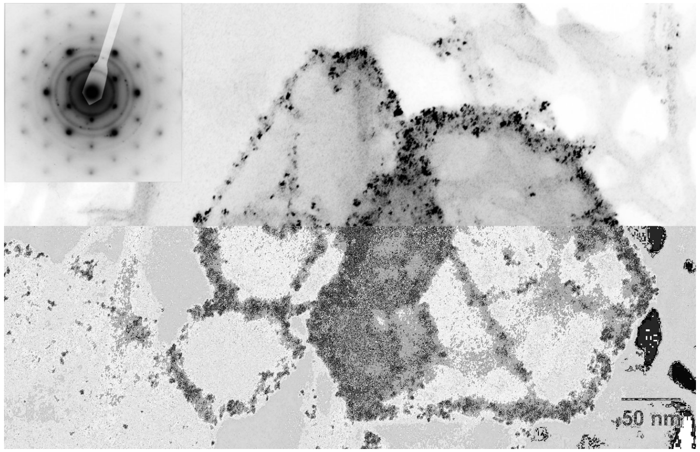


Particle size from U-U coordination



Modeling of EXAFS U-GR$_{SO_4}$ data predicted ~1-2 nm UO_2 particles





TEM imaging revealed nanoscale UO_2 particles (~2-5 nm)

Summary

Lepidocrocite Bioreduction

- Variability in lepidocrocite bioreduction among *Shewanella* species
- Broad range of *Shewanella* species can form green rust
- Carbonate green rust dominant product with formate, H_2, lactate, and *N*-acetylglucosamine
- Siderite dominant product with serine and pyruvate

U(VI) reduction

- U(VI) reduced to U(IV) in presence of biogenic green rust
- Molecular clusters of uraninite-like U(IV) in close association with Fe
- Results similar for green rusts formed by different species
- Biogenic green rust may be a reactive phase for contaminant reduction in Fe(III)-reducing environments

For all this and MORE, see our poster TONIGHT!